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First-principles Theory and Calculations of Electronic g-tensor Elements for Paramagnetic Defects in Semiconductors and Insulators

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Geometries, Vertical Excitation Energies, Hyperfine Coupling Constants and Electronic g-tensor Elements for Small Gallium Arsenide Clusters, Ga_xAs_y (x + y = 3, 5)

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Abstract

The g-tensors (2nd order) of doublet radical gallium arsenide clusters Ga_xAs_y (x + y = 3, 5), were calculated from first principles using new packages. Geometry optimizations and hyperfine coupling constants are also reported, using the B3LYP/6-311+g(2df) level. ESR results were compared to experimental Ga_2As_3 data, and previous calculations for Ga_2As, $GaAs_2$, Ga_2As_3. New ESR and structural results are presented for $GaAs_4$ and Ga_4As. Our results for Ga_2As_3, the only Ga-As cluster for which experimental ESR data exist, were a better fit to experimental values than previous calculations, implying our Δg results for the other Ga_xAs_y clusters are also of good quality.

1. Introduction

To date there have been few experimental ESR studies on III-V doublet radicals, namely only on BNB[1] and Ga_2As_3 [2] to our knowledge. For triplet or quartet III-V radicals, experimental ESR data have only been found for $GaAs^+$ ($X^4\Sigma^-$),[3] GaP^+ ($X^4\Sigma$),[4] GaAs-$Al_xGa_{1-x}As$,[5] antisite defects (P_{Ga} in GaP,[6] As_{Ga} in GaAs,[7] and P_{In} in InP [8]), and Ga-vacancies in electron-irradiated GaP.[9]

However there have been a number of theoretical studies on the electronic states and structures of III-V radicals, in particular for Ga-As containing neutral and ionic doublet radicals.[10-22] Arratia-Pérez and Hernández-Acevedo[12] calculated the magnetic Zeeman and hyperfine interactions of Ga_2As_3 using the self-consistent Dirac scattered wave method (SCF-DSW-Xα) of Yang *et al*[23] and a first-order perturbation procedure, which confirmed Weltner's[2] ESR spectral determination of a trigonal bipyramidal structure for Ga_2As_3. Arratia-Pérez and Hernández-Acevedo have also calculated the magnetic Zeeman and hyperfine interactions for $GaAs_2$ and Ga_2As,[13] although to date there are no experimental ESR data for these species.

We compare these calculated and experimental data to our results, and also use the g-tensor results as a launching point to the study of larger clusters which approach bulk properties, with and without site defects.

2. Methods

Geometry optimizations and hyperfine coupling constant (hfcc) calculations were carried out with the GAUSSIAN 98 suite of programs[24] at the B3LYP/6-311+G(2df) level. Starting geometries were those given in the literature for $GaAs_2$,[14,17] Ga_2As,[17,19] Ga_2As_3 and Ga_3As_2,[19,25] $GaAs_4$ and Ga_4As,[15] with other possible geometries also examined. For $GaAs_4$ and Ga_4As, only sketches of the structures were provided.[15]

The theoretical evaluation of g-tensors using perturbation theory is described in detail in refs. 26 and 27. The total Δg for a given molecule is comprised of first- and second-order terms. In this paper, only second-order g-tensor components were calculated, as the first-order contributions to the total Δg are expected to be

very small (*ca.* 100 ppm) in relation to the second order Δg values. The contribution to Δg (2^{nd}) is due to the coupling of an excited state with the ground state, and is proportional to their spin-orbit coupling (SO) and magnetic transition moment (L) matrix elements, and inversely proportional to their energy separation (ΔE). The total second-order Δg is calculated as a sum-over-states expansion, which generally involves strong coupling to only the first few low-lying excited states.[28-30]

Programs developed earlier in this group[27] worked very well for 1st and 2nd order g-tensor calculations (*e.g.* refs. 27 - 30) but were limited to systems with up to *ca.* 80 electrons. Ga-As containing clusters, the focus of this paper, quickly surpassed this limitation. Also, speed is an issue if the calculation of larger clusters is to be practical. New programs were acquired and modified for our purposes to calculate the g-tensors of these Ga-As clusters. They are based on: the Turbomole package[31] for efficient integral and SCF calculations; on the Grimme multireference CI (MRCI) package,[32] which also gives the angular momentum (L) matrix elements that we require; and finally on the Marian-Hess mean-field spin-orbit integrals[33] as implemented by Schimmelpfennig,[34] and adapted for the Grimme MRCI package by Marian and Kleinschmidt.[35] Here the one- and two-electron spin-orbit elements are calculated from an effective one-electron, one-center mean-field approximation. Therefore the spin-orbit matrix elements, which in full *ab initio* mode require large amounts of computer time, can be calculated in much less time but are not as accurate.

The electronic charge centroid (ECC) was taken as gauge origin.[36]

Test results with the new package gave g-shifts within 15 - 20 % of MRCI[37] values for small molecules containing first- and second-row atoms (*e.g.* AlO, H_2CO^+; LiC_2).[38] With the new package, the following III-V doublet radicals were studied: $GaAs_2$ (97 electrons), Ga_2As (95 e), Ga_2As_3 (161 e), Ga_3As_2 (159 e), $GaAs_4$ (163 e), and Ga_4As (157 e).

3. Optimized geometries

All geometry optimizations were done at the B3LYP/6-311+g(2df) level of theory. The results for the lowest energy structures are given in Table 1, and compared with those of previous calculations. The various structures are shown in Figure 1.

3.1. $GaAs_2$

$GaAs_2$ was first examined in 1987,[20] and again in 2000[17] by Balasubramanian as a triangular C_{2v} structure; a 1991 study also considered a linear $C_{\infty v}$ geometry.[16] Work by Meier *et al* in 1991[14] examined triangular C_{2v} and linear ($D_{\infty h}$, $C_{\infty v}$) geometries. In all cases, the ground state was $^2B_2$ with a C_{2v} triangular geometry.

Our results also gave X^2B_2 in C_{2v} symmetry as the lowest energy state. Alternate possible geometries considered here for $GaAs_2$ were linear $D_{\infty h}$ ($X^2\Pi_g$, As-Ga-As: Ga-As = 2.22 Å) and $C_{\infty v}$ ($X^2\Pi$, Ga-As-As: Ga-As = 2.48 Å, As-As = 2.16 Å) structures that were 1.62 and 0.52 eV, respectively, higher in energy than X^2B_2 (Figure 1). This compares well to the results of Meier *et al*,[14] where X^2B_2 was lower than the $D_{\infty h}$ (2.39 Å) and $C_{\infty v}$ (Ga-As = 2.61 Å, As-As = 2.24 Å) structures by 1.53 and 0.81 eV, respectively.

3.2. Ga_2As

For Ga_2As, Balasubramanian reported an X^2B_2 ground state with C_{2v} symmetry and an angle of 79.9°, with a C_L ($^2A'$) structure (Ga-As = 2.283, 2.534 Å; Ga-As-Ga = 90.3°) 0.025 eV higher in energy (MRCI+Q, where Q was defined as multireference Davidson corrections to the MRCI energies for uncoupled quadruple clusters).[17] Two other low lying states, $^2B_1$ (2.52 Å, 108.2°, ΔE = +0.22 eV) and $^2A_1$ (2.47 Å, 118.5°, ΔE = +0.19 eV), were also reported in ref.17. Balasubramanian found a $^2B_1$ ground state in his 1991 study.[16]

Our attempts to reproduce Balasubramanian's C_{2v} (X^2B_2) geometry from ref. 17 (2000) resulted instead in an Ga-As-Ga angle of *ca.* 96 degrees [for the 6-311+g(2df) basis set, B3LYP gave Ga-As 2.384 Å,

96.3°; MPW1PW91 gave 2.358 Å, 93.3°; and MP2 gave 2.365 Å, 103.5°] for Ga_2As, in close agreement with the local spin density (LSD) result of 98.0° from ref. 19 (see Table 1). Our linear $D_{\infty h}$ ($X^2\Pi_u$, 2.447 Å) and $C_{\infty v}$ ($X^2\Pi$, As-Ga = 2.246 Å, Ga-Ga = 2.665 Å) structures were 0.09 and 0.84 eV higher in energy, respectively, than our X^2B_2 C_{2v} bent geometry. In Balasubramanian's 1991 paper with the $^2B_1$ ground state,[16] the ordering was C_{2v} (X^2B_1: 2.527 Å, 109.5°) 0 eV; $D_{\infty h}$ (2.498 Å) +0.12 eV; $C_{\infty v}$ (As-Ga = 2.319 Å, Ga-Ga = 2.735 Å) +0.68 eV.

3.3. Ga_2As_3

The structure of Ga_2As_3 was predicted in 1992 to be a D_{3h} trigonal bipyramid with an $X^2A_2"$ ground state, using the LSD method.[19] The ESR spectrum was obtained one year later, from which a trigonal bipyramidal structure was proposed.[2] MRCI calculations by Liao *et al*,[25] and HF followed by MP2 calculations by Piquini *et al*,[15] also resulted in D_{3h} trigonal bipyramidal structures.

Our calculations showed the lowest energy structure of Ga_2As_3 to have an $X^2A_2"$ ground state with D_{3h} trigonal bipyramidal geometry, in agreement with the structure proposed from the experimental ESR data[2] and previous calculations.[15,19,25] Alternate possible geometries considered by us, shown in Figure 1, were: a C_{2v} square pyramid (X^2B_1), 0.97 eV higher than the D_{3h} structure; and a C_s square pyramid ($X^2A"$, two Ga in the 'base') 0.46 eV higher in energy.

3.4. Ga_3As_2

CASSCF and MRCI calculations by Liao *et al*,[25] using relativistic effective core potentials (RECP), showed two nearly degenerate isomers for Ga_3As_2: a distorted C_{2v} trigonal bipyramid (X^2A_1, C_{2v} (a) in Figure 1), and a C_s edge capped tetrahedron (X^2B_1, C_s (b) in Figure 1), with the C_{2v} trigonal bipyramid being lower in energy by 0.005 eV (MRCI + Q, and 0.03 eV CASSCF). LSD calculations by Lou *et al* gave similar results, with an energy separation of 0.01 eV.[19]

For Ga_3As_2, we also found that the lowest energy geometry was not D_{3h} as for Ga_2As_3, but rather a C_{2v} distorted trigonal bipyramid having a $^2A_1$ ground state with the equatorial Ga atoms arranged in an isosceles triangle; the energy gap between the C_{2v} and D_{3h} geometries was 0.13 eV (0.1 eV in ref. 19). Other geometries we investigated (see Figure 1) were a C_{2v} edge-capped tetrahedron [X^2B_1, C_{2v} (b) in Figure 1] 0.16 eV higher in energy; a C_s square pyramid (X^2A'', two As in the 'base') 0.64 eV higher in energy; and a C_{2v} square pyramid [X^2A_1, C_{2v} (c) in Figure 1], 1.36 eV higher than the C_{2v} distorted trigonal bipyramid [C_{2v} (a)].

3.5. $GaAs_4$

$GaAs_4$ was included in a study of electronic and structural trends in small GaAs clusters by Piquini *et al*, who carried out Hartree-Fock SCF calculations including all electrons and no symmetry constraints during optimization, followed by single-point MP2 calculations on the minimum energy configurations.[15] However, they did not report any geometry details other than a sketch of the molecule, the symmetry, and a table of selected bond orders.

Our results gave a C_{2v} edge-capped tetrahedron [X^2B_2, C_{2v} (a) in Figure 1] as the lowest energy structure, resembling that shown in ref. 15. We calculated C_{4v} square pyramidal (X^2A_1) and C_{2v} planar trapezoidal [X^2B_1, C_{2v} (b) in Figure 1] geometries to be 0.30 and 1.68 eV, respectively, higher in energy than the C_{2v} edge-capped tetrahedron.

3.6. Ga_4As

Ga_4As was also included in the study by Piquini *et al*,[15] and again no detailed geometrical information was given. The lowest energy structure we obtained for Ga_4As was a C_{2v} planar trapezoidal structure (X^2A_1) with the As atom in the center [C_{2v} (a) in Figure 1], similar to the structure obtained by Piquini *et al*.[15] Our results showed square pyramidal (C_{4v}, X^2B_1) and C_{2v} edge-capped tetrahedral [X^2A_2, C_{2v} (b) in Figure 1] geometries to be respectively 0.23 and 0.56 eV higher in energy than the planar trapezoidal structure.

4. Hyperfine coupling constants

The atomic charges, spin densities (SD) and hfcc data are given in Table 2. For all six molecules, the Ga atoms carry positive charges and all As atoms are negatively charged, as expected since As is more electronegative than Ga. The SOMOs are shown in Figure 2.

4.1. $GaAs_2$

The SOMO of $GaAs_2$ is composed of an in-phase combination of a Ga p_y orbital with As p_z orbitals, forming σ-type antibonding orbitals along each Ga-As bond, as also reported in ref. 13. These Ga-As antibonding orbitals of the SOMO are *ca.* parallel to the *z*-axis, perhaps due to the small As-As distance (2.193 Å) which is slightly shorter than that calculated for As_2^+ (2.30 Å) and As_2^- (2.31 Å).[14]

The SD is greater on the As atoms (0.368 per atom) than on the Ga atom (0.262). This is in good agreement with the spin populations calculated in ref. 13, who report 0.338 (0.106 isotropic, 0.232 anisotropic) per Ga and 0.331 (0.121 isotropic, 0.210 anisotropic) per As atom. The anisotropic spin-dipolar couplings ($T_{xx,yy,zz}$ in Table 2) are much larger than A_{iso} for both Ga and As, and the relative magnitudes of our spin-dipolar couplings are similar to those from ref. 13 (see Table 2).

4.2. Ga_2As

The SOMO is formed from an in-phase combination of a p_x orbital from all three atoms according to ref. 13, but this corresponds to the SOMO-1 in our calculations: our SOMO is comprised of three in-plane p-orbitals: p_z on As and the p_σ orbitals of Ga lie along the As-Ga bonds such that the negative lobes for all three orbitals point toward the center of the molecule. Our geometry differs slightly from that used in ref. 13; this could be the cause of the different SOMOs, and would also affect the g-tensor calculations (see below).

More than half of the SD in Ga_2As resides on the As (0.515), with 0.242 per Ga atom. A similar trend is reported in ref. 13, but with more SD on the apical As atom: 0.694 per As and 0.153 per Ga, with larger

anisotropic than isotropic SD contributions for each atom. A_{iso} is largest for the Ga atoms, and the spin-dipole couplings ($T_{xx,yy,zz}$) are smaller for Ga than As, similar to the results from ref. 13.

4.3. Ga_2As_3

Our results place the majority of the SD on the Ga atoms (0.369), with only 0.088 per As atom. This agrees with the SD distribution from ref. 12 (0.314 per Ga, 0.124 per As). Based on the experimental results it was estimated that the unpaired electron was mainly confined to pσ orbitals on the axial gallium atoms.[2] This estimation is not supported by the SOMO (as also noted in ref. 12), which shows sizeable in-phase π-bonding between the equatorial As atoms via p_z orbitals, and p_σ antibonding between Ga and As atoms.

Our A_{iso} differs from the experimental $^{69}Ga_2As_3$ (Ar matrix)[2] result by 13%. Ref. 12 reports calculated A_{iso} values for only ^{71}Ga, even though the natural abundance is 60.4% ^{69}Ga and 39.6% ^{71}Ga; their A_{iso} value is almost identical to the derived experimental $^{71}Ga_2As_3$ result. The experimental results were derived assuming $g_\parallel = g_e$, and $A_\parallel \cong A_\perp \cong A_{iso}$ for As.[2] This does not appear to be valid, based on results from ref. 12 where anisotropic spin distributions for the As atoms were calculated to be *ca.* twice the isotropic spin distribution.

4.4. Ga_3As_2

The small distortion from D_{3h} to C_{2v} symmetry makes a significant impact on the SD and charges of the Ga atoms in Ga_3As_2, as well as the SOMO. The SOMO is composed of in-phase p_y orbitals on Ga_1 and the As atoms, with p_σ orbitals on Ga_2 and Ga_3 oriented to form Ga_2-As and Ga_3-As antibonds. The SD is four times larger, and the charge is two times smaller, for the Ga_1 atom (Table 2) than for Ga_2 and Ga_3. The A_{iso} for Ga_1 is much larger than for Ga_2 and Ga_3, and the SD, charge, A_{iso}, and anisotropic ($T_{xx,yy,zz}$) hfcc values for Ga_1 are all similar to that for each of the Ga atoms in Ga_2As_3.

4.5. $GaAs_2$

The SOMO of $GaAs_4$ lies in the yz-plane from p_y orbitals on all atoms; the orbitals on Ga, As_1 and As_2 are in-phase, and of opposite phase to those on As_3 and As_4.

The majority of SD lies on As_1 and As_2 (see Figure 1), with very little on the other three atoms. This is reflected in the larger A_{dip} values for these atoms (Table 2), which are an order of magnitude larger for As_1 and As_2 than for As_3 and As_4.

4.6. Ga_4As

The SOMO lies in the plane of the molecule, with p_y orbitals of Ga_1 and Ga_2 oriented to be bonding between Ga_1-Ga_2, with the pσ orbitals of Ga_4 and Ga_5 positioned to be Ga_1-Ga_5 and Ga_2-Ga_4 antibonding. The p_z orbital on As is small and is oriented to be in phase with the p_y orbitals between Ga_1 and Ga_2.

There is almost no SD associated with the As atom in Ga_4As, but the largest atomic charge resides on As (-0.509). Most of the SD resides on Ga_1 and Ga_2, and is *ca.* twice the SD for Ga_3 and Ga_4; whereas the charges on Ga_1 and Ga_2 is ca. half that for Ga_3 and Ga_4. This inverse relationship between charge and SD was observed by Bruna and Grein for alkali-metal diatomic radical cations.[30]

5. G-tensors

In Table 3, the types of excited states that couple with four different ground states in C_{2v} symmetry (X^2A_1, X^2A_2, X^2B_1, X^2B_2) are listed. Table 4 summarizes our total Δg (2nd order) values and compares them to known experimental and theoretical results. To our knowledge there are no experimental or calculated ESR data for Ga_3As_2, $GaAs_4$, or Ga_4As. For all Ga_xAs_y doublet radicals ($x + y = 3, 5$) ΔE, SO, L and Δg values for the first five excited states for each irreducible are given in Tables 5 - 10, and results for higher excited states if they have a strong magnetic coupling with the ground state. Fifteen excited states were calculated for Ga_3As_2, $GaAs_4$ and Ga_4As since significant magnetic coupling with the ground state was still observed in the higher states of initial 9-root calculations. Tables 5 - 10 can also be used for vertical excitation energies, which

are given in the body of the table or as a footnote.

All C_{2v} molecules have the *z*-axis along the C_2 symmetry axis. $GaAs_2$ and Ga_2As are placed in the *yz*-plane.

5.1. $GaAs_2$

Table 5 shows that Δg_{xx} for $GaAs_2$ is governed by the coupling of 1^2A_1 ($4a_1 \rightarrow 2b_2$, SOMO-1 to SOMO) and 2^2A_1 ($3a_1 \rightarrow 2b_2$, SOMO-3 to SOMO) with X^2B_2.

The Δg_{yy} component is dominated by the coupling with 1^2A_2 ($2b_2 \rightarrow 2b_1$), SOMO to LUMO+1. There are also strong couplings with 2^2A_2 and 3^2A_2 but they almost cancel each other: their individual Δg_{yy} contributions are similar in magnitude and opposite in sign. This is a general trend observed for a pair of states generated by a three open shell configuration,[28,39,40] *e.g.* for H_2CO^+ the ΔE, SO and L values for the $1,2^2A_2$ states (Δg_{yy}) were of similar magnitude but their contributions to Δg were of opposite sign.[28] In the case of $GaAs_2$, the ΔE and SO values for 2^2A_2 and 3^2A_2 are similar, but the L values differ by *ca.* 50% (15% deviation in L values in the H_2CO^+ example[28]). This variation of the L values may occur since although the leading configuration for both 2^2A_2 and 3^2A_2 is a $4a_1 \rightarrow 2b_1$ excitation (90% and 85%, respectively), there are small differences in the other configurations contributing to 2^2A_2 and 3^2A_2 (Table 5).

The total Δg_{zz} component is an order of magnitude smaller than Δg_{xx} and Δg_{yy}. Although the strongest couplings with X^2B_2 arise from 5^2B_1 and 6^2B_1, their Δg contributions almost cancel each other, since both of these states derive from a three open shell configuration[28,39,40] ($3a_1 \rightarrow 1a_2$, SOMO-3 to LUMO). In this case the ΔE for the two states are very close, but the SO and L values differ by *ca.* 50%. These differences arise from mixing of the leading configuration.

Calculated g-shifts for $GaAs_2$ by Arratia-Perez *et al*[13] utilized a first-order perturbation procedure based on the SCF-DSW-Xα method,[23] and a geometry by Lou *et al.*[18,19] Although three g-components are expected for C_{2v} symmetry, they give only $\Delta g_\parallel$ and $\Delta g_\perp$ values. Assuming their $\Delta g_\parallel$ is along As-As (Δg_{yy}) and

$\Delta g_\perp$ is Δg_{xx}, our calculated Δg values for $GaAs_2$ differ significantly from those calculated in ref. 13, being *ca.* 70000 ppm larger in magnitude. There is no experimental ESR data available for $GaAs_2$ to gauge the accuracy of either result.

5.2 Ga_2As

The Δg_{xx} value of Ga_2As is not dominated by coupling with any one excited state; rather 1^2A_1 - 4^2A_1 all make large negative contributions to Δg_{xx}, countered to a small extent by 6^2A_1 (Table 6).

The two largest contributions to Δg_{yy} are negative values from 2^2A_2 and 4^2A_2, countered by a positive one from 5^2A_2. As the leading configurations for 4^2A_2 and 5^2A_2 are the same ($3a_1 \rightarrow 2b_1$), the ΔE and L values are similar and their Δg contributions are of opposite sign, but the SO values differ by *ca.* 50%. This is due to 5^2A_2 being dominated by a three open shell configuration ($3a_1 \rightarrow 2b_1$), whereas 4^2A_2 is more evenly comprised of this (40 %) and a double excitation from the SOMO-1 to the SOMO and LUMO+1 ($3a_1^2 \rightarrow 2b_2 1a_2$) (37 %).

The Δg_{zz} value is dominated by coupling to 1^2B_1, with contributions from $3,5,6^2B_1$. The 5^2B_1 and 6^2B_1 states have the same leading three open shell configuration, SOMO-1 ($3a_1$) to the LUMO+2 ($1a_2$), but again the Δg contributions from these two states do not cancel[28,39,40] due to differences in the configuration setup.

As with $GaAs_2$, only $\Delta g_\parallel$ and $\Delta g_\perp$ values for Ga_2As are given in ref. 13. If we assume that their $\Delta g_\parallel$ is along Ga-Ga (*y*-axis, as for $GaAs_2$ along As-As), then the Δg_{yy} comparison is very poor. If their $\Delta g_\parallel$ corresponds instead to Δg_{zz}, then the result differs from ours by *ca.* 20%, but is inconsistent with the $GaAs_2$ *x,y,z*-axis assignments.

5.3. Ga_2As_3

In D_{3h} symmetry (X^2A_2''), the standard orientation places the Ga atoms of Ga_2As_3 along the *z*-axis, with the As atoms in the *xy*-plane; *x* and *y* (and Δg_{xx} and Δg_{yy}) are degenerate ($^2E'$). Our Δg calculations were done

with Ga_2As_3 in C_{2v} symmetry (X^2B_1), placing the Ga atoms along the *x*-axis and the As atoms in the *yz*-plane with one As atom lying on the *z*-axis. In this case, the $^2A_1$ and $^2B_2$ states correspond to $^2E'$. For checking the accuracy of our calculations, we calculated Δg for both $^2A_1$ and $^2B_2$ states. The degenerate components of Δg will always be called Δg_{xx} and Δg_{yy}, corresponding to the D_{3h} notation. Due to the independent selection of reference configurations and extrapolation for $^2A_1$ and $^2B_2$ states, slightly different values were obtained for Δg_{xx} and Δg_{yy}.

The degree of degeneracy of Δg_{xx} and Δg_{yy} can be checked in Table 7. The values are dominated by coupling of the ground state with 3^2A_1 and 2^2B_2, respectively, corresponding to excitation from the SOMO ($3b_1$) to the degenerate LUMO ($6a_1$) for Δg_{xx} and LUMO+1 ($3b_2$) for Δg_{yy}. The second largest contribution is from 5^2A_1, an excitation from the SOMO to the degenerate LUMO+4 ($7a_1$), and from 4^2B_2, SOMO to LUMO+3 ($5b_2$). The remaining major excited state couplings involve $6,7^2A_1$ and $5,6^2B_2$, excitations from the degenerate SOMO-2 ($1a_2$, Δg_{xx}) and SOMO-1 ($2b_1$, Δg_{zz}) to the LUMO+2 ($4b_2$), resulting in three open shell configurations. As shown in Table 7 for Δg_{yy}, the ΔE, SO and L values for 5^2B_2 and 6^2B_2 are very similar and the Δg values are opposite in sign. This behaviour is expected for pairs of states generated by a three open shell configuration.[28,39,40] This is not as evident in 6^2A_1 and 7^2A_1 in Δg_{xx}, where the SO and L values are similar, but the ΔE values differ by 1.1 eV.

As shown in Table 7, Δg_{xx} was calculated to be an order of magnitude smaller than Δg_{yy} and Δg_{zz}, with the largest contribution from coupling with the 3^2A_2 state, an excitation from SOMO-5 ($4a_1$) to LUMO+2 ($4b_2$).

Ga_2As_3 is the only Ga_xAs_y doublet radical with published experimental ESR data; comparison of our results to the experimental[2] and published theoretical[12] g-tensor data is given in Table 4. Our results are in good agreement with experiment,[2] being a much closer fit than the theoretical results from ref. 12.

5.4. Ga_2As_2

In our calculations the three Ga atoms of Ga_3As_2 were placed in the *yz*-plane and the two As atoms along the *x*-axis. The distortion from a D_{3h} trigonal bipyramid to C_{2v} symmetry was accomplished by having the Ga_1-Ga_2 (and Ga_1-Ga_3) distance shorter than Ga_2-Ga_3 [See Figure 1, C_{2v} (a)] . Ga_1 lies along the *z*-axis, Ga_2 and Ga_3 along *y*.

The Δg_{xx} value is governed by the coupling of 1^2B_2 and 3^2B_2 with the X^2A_1 ground state (Table 8).

There are numerous contributions to Δg_{yy}, the largest being 1^2B_1 ($2b_1 \rightarrow 5a_1$, SOMO-3 to SOMO) and 3^2B_1 ($5a_1 \rightarrow 3b_1$, SOMO to LUMO+2), which almost cancel each other. The overall Δg_{yy} is relatively small, with most of the small negative contributions ($2,4,6,14^2B_1$) being negated by positive contributions from 5^2B_1 and 11^2B_1.

The overall Δg_{zz} is also small, due to cancelling contributions from pairs of states generated by three open shell configurations. Contributions to Δg_{zz} from 2^2A_2 and 3^2A_2, both having the same configuration, almost cancel each other: their ΔE values are almost identical, and although the SO of 2^2A_2 is *ca.* 70% larger than that of 3^2A_2, the L value for 2^2A_2 is *ca.* 80% smaller than that of 3^2A_2. The leading configuration for 4^2A_2 and 5^2A_2 is the same ($1a_2 \rightarrow 6a_1$, SOMO-2 to LUMO+1), but the respective Δg's differ vastly in magnitude, due probably to some mixing of configurations.

5.5. $GaAs_4$

The molecule was oriented such that Ga lies on the *z*-axis, and As_1-As_2 in the *yz*-plane; As_3 and As_4 lie in the *xz*-plane [Figure 1, C_{2v} (a)].

For Δg_{xx}, magnetic coupling was dominated by coupling with 1^2A_1 ($3b_2 \rightarrow 6a_1$, SOMO to LUMO). Large negative contributions from $2,5^2A_1$ are effectively cancelled by $4,9^2A_1$ (Table 9).

In contrast to Δg_{xx}, the overall Δg_{yy} and Δg_{zz} values were small due to cancelling positive and negative Δg components from numerous excited states. For Δg_{yy}, large contributions from 1^2A_2 and 2^2A_2 are of opposite (three open shells) and nearly cancel. The next largest contributions arise from 5^2A_2 and 10^2A_2, both being

positive. However, the overall Δg_{yy} is relatively small and negative due to negative contributions from a number of states ($3,4,6,7,9,11^2A_2$).

The largest contributions to Δg_{zz}, from 1^2B_1 and 2^2B_1, are again of opposite sign although the two states do not derive from the same configuration. Next largest in magnitude are contributions from 8^2B_1 and 11^2B_1, which have the same three open shell configuration. Due to other contributing states, the final Δg_{zz} is again relatively small.

5.6. Ga_4As

In our calculations Ga_4As was in the *yz*-plane, with the *z*-axis bisecting the Ga_2-As-Ga_3 and Ga_4-As-Ga_5 angles (see Figure 1); the *x*-axis was perpendicular to the molecular plane.

For Δg_{xx}, the magnetic coupling was dominated by two excited states ($1,2^2B_2$), the leading configurations for which were the same ($5a_1 \rightarrow 4b_2$ and $3b_2 \rightarrow 5a_1$) but contributed in an approximately opposite manner (1^2B_2: 62% and 29%; 2^2B_2: 29% and 63%, respectively, see Table 10).

The largest contributions to Δg_{yy} were from high-lying excited states ($6,7,8^2B_1$). All of the states contributing significantly to Δg_{yy} had negative Δg components with the exception of 5^2B_1, which is one of a pair of states (with 6^2B_1) from a three open shell configuration ($4a_1 \rightarrow 2b_1$).

High-lying states also dominate Δg_{zz}, with the largest negative contributions from $6,7,12,14^2A_2$. The largest positive Δg contribution is from 11^2A_2, which has the same three open shell configuration as 12^2A_2 ($3b_2 \rightarrow 3b_1$), although neither state is dominated by this configuration (42% for 11^2A_2, 60% for 12^2A_2). The other state with a positive contribution to Δg_{zz} is 4^2A_2, which has the same leading three open shell configuration as 6^2A_2 ($3b_2 \rightarrow 2b_1$); here the SO values are quite different and the ΔE's differ by *ca.* 1 eV, and two Δg contributions are opposite in sign but are not similar in magnitude.

6. Summary and Conclusions

New programs developed for the calculation of g-tensors, based on multireference CI wavefunctions, have been capable of determing g-tensors for III-V doublet radicals with up to 163 electrons in an efficient manner, and without the need for RECPs (although this may still be necessary for the study of larger clusters).

In contrast to smaller molecules for which strong magnetic coupling with the ground state is observed with only a few excited states (*e.g.* refs. 28-30), significant contributions to Δg were often observed from various higher excited states of Ga_xAs_y. This is due in part to the higher energy-density of excited states of these molecules, *e.g.* 14 excited states are within 4 eV for Ga_4As (Δg_{zz} in Table 10).

From comparison with experimental ESR data for Ga_2As_3 [2] (Table4) it is evident that our new g-tensor results are significantly better than the DFT results reported in ref. 12, although they correctly reproduced the trends of the experimental results (*i.e.* $\Delta g_{xx} << \Delta g_{yy}, \Delta g_{zz}$). This suggests that our g-tensor results for $GaAs_2$ and Ga_2As are also improved over published DFT values,[13] and that results for the other clusters are reliable. Future work includes using these new programs to investigate the structures and properties of larger III-V clusters (11+ atoms), and the study of paramagnetic defects (heteroatomic,[5] anti-site[6-8] and hole defects[9]) within these larger clusters. Results presented in this paper show that one does not need to consider all valence electrons (VE), which decreases calculation times and may allow larger molecules to be calculated before the use of RECPs is required.

Also planned are modifications to the program code to allow g-tensor calculations for triplet and quartet multiplicities. A number of AB⁻ III-V compounds for which experimental ESR data are available (*e.g.* $GaAs^+$,[3] GaP^+ [4]) have quartet ground states. Higher spin states are not restricted to ions, e.g. GaP_3 has a $^3A_2$ ground state.[41] These would be helpful in gauging the quality of our results, since to our knowledge Ga_2As_3 [2] and BNB[1] are the only III-V doublet radicals with published ESR data.

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Table 1. Optimized bond distances (Å) and angles (deg) from this work [B3LYP/6-311+G(2df)], and comparison to literature values, for all Ga_xAs_y (x + y = 3, 5) doublet radicals.

Molecule, symmetry, ground state	Results		
$GaAs_2$ C_{2v}, X^2B_2	This work	Ref. 17 (MRCI)	Ref. 14 (MRCI)
Ga-As	2.775	2.80	2.86
As-Ga-As	46.5	45.9	46.6
Ga_2As C_{2v}, X^2B_2	This work	Ref. 17 (MRCI)	Ref. 19 (LSD)
Ga-As	2.384	2.407	2.33
Ga-As-Ga	96.3	79.9	98.0
Ga_2As_3 D_{3h}, $X^2A_2"$	This work	Ref. 25 (MRCI)	Ref. 19 (LSD)
Ga-Ga	4.268	not reported	not reported
Ga-As	2.594	2.589	2.65
As-As	2.555	2.563	2.62
Ga_3As_2 C_{2v}, X^2A_1	This work	Ref. 25 (MRCI)	Ref. 19 (LSD)
Ga_1-Ga_2, Ga_1-Ga_3[a]	3.751	3.702	3.72
Ga_2-Ga_3	3.979	4.114	4.57
Ga_1-As_1	2.446	2.401	2.41
Ga_2-As_1, Ga_3-As_1	2.671	2.725	2.59
As_1-As_2	2.725	2.782	2.70
Ga_2-Ga_1-Ga_3	64.0	67.5	70.0
As_1-Ga_1-As_2	67.7	70.8	67.9
As_1-Ga_2-As_2, As_1-Ga_3-As_2	61.3	61.4	55.2

Table 1 continued.

$GaAs_4$ C_{2v}, X^2B_2	This work	Ref. 15
$Ga\text{-}As_1$, $Ga\text{-}As_2$[a]	**3.116**	**no data given:**
$Ga\text{-}As_3$, $Ga\text{-}As_4$	2.545	C_{2v}, edge-capped
$As_1\text{-}As_3$, $As_1\text{-}As_4$, $As_2\text{-}As_3$, $As_2\text{-}As_4$	2.454	tetrahedron
$As_1\text{-}As_2$	3.006	
Ga_4As C_{2v}, X^2A_1	This work	Ref. 15
$Ga_1\text{-}As$, $Ga_2\text{-}As$[a]	2.588	no data given:
$Ga_3\text{-}As$, $Ga_4\text{-}As$	2.487	C_{2v}, planar
$Ga_1\text{-}Ga_3$, $Ga_2\text{-}Ga_4$	2.870	trapezoid
$Ga_1\text{-}Ga_2$	2.599	with As in center
$Ga_1\text{-}Ga_4$, $Ga_2\text{-}Ga_3$	4.583	
$Ga_3\text{-}Ga_4$	4.913	
$Ga_1\text{-}As\text{-}Ga_2$	60.3	
$Ga_1\text{-}As\text{-}Ga_3$, $Ga_2\text{-}As\text{-}Ga_4$	68.8	
$Ga_1\text{-}As\text{-}Ga_4$, $Ga_2\text{-}As\text{-}Ga_3$	129.1	
$Ga_3\text{-}As\text{-}Ga_4$	162.0	

a See Figure 1 for atom labelling scheme.

Table 2. Spin densities, atomic charges, and hyperfine coupling constants (MHz) for all Ga_xAs_y ($x + y = 3, 5$) doublet radicals.

Molecule	Atom	Spin Density[a]	Charge[a]	A_{iso}	T_{xx} / T_{yy} / T_{zz} [b]
$GaAs_2$ C_{2v}, X^2B_2	**Ga**	**0.262**	**0.226**	**26**	**-57 / 131 / -74**
Ref. 10		0.338	0.193		83[d]
	As	0.368	-0.113	7	-111 / -113' / 225'
Ref. 10		0.331	-0.096		125[d]
Ga_2As C_{2v}, X^2B_2	Ga	0.242	0.128	447	-63 / -81' / -63'
Ref. 10		0.153	0.103		27[d]
	As	0.515	-0.257	-148	-159 / 304 / -145
Ref. 10		0.694	-0.206		216[d]
Ga_2As_3 D_{3h}, X^2A_2''	Ga	0.369	0.194	1325[c]	-65 / -65 / 129
Ref. 9		0.314	0.150		81[d]
	As	0.088	-0.129	-23[c]	-35 / -36 / 71
Ref. 9		0.124	-0.100		14[d]
Ga_3As_2 C_{2v}, X^2A_1	Ga_1	0.426	0.175	1735	-85 / -71 / 156
	Ga_2, Ga_3	0.085	0.276	203	-21 / 45' / -24'
	As_1, As_2	0.202	-0.363	-25	-61' / -56 / 116'
$GaAs_4$ C_{2v}, X^2B_2	Ga	-0.038	0.214	-153	4 / 17 / -21
	As_1, As_2	0.585	-0.078	-46	-156 / 308' / -152'
	As_3, As_4	-0.066	-0.030	12	-10' / 45 / -36'
Ga_4As C_{2v}, X^2A_1	Ga_1, Ga_2	0.342	0.083	-122	-89 / 177' / -88'
	Ga_3, Ga_4	0.169	0.171	153	-34 / -43' / 76'
	As	-0.021	-0.509	0.05	-13 / -7 / 20

a Atomic charges from a Mulliken population analysis.

b Off-diagonal spin-dipolar (anisotropic) coupling terms T'_{xx}, T'_{yy}, T'_{zz} are indicated by a ' after the value.

c A_{iso} = 1524 [1936] MHz, A_{dip} = 87 [71] MHz from experimental ESR spectra for $^{69}Ga_2As_3$ [$^{71}Ga_2As_3$].[2] A_{iso} = 2012 Mhz, A_{dip} = 88 Mhz for $^{71}Ga_2{}^{75}As_3$ in ref. 12.

d The spin-dipolar contribution to hfcc from ref. 13, defined as the expectation value $(3x^2 - \mathbf{r}^2)/\mathbf{r}^5$ averaged over the relativistic wave function.

Table 3. Excited state couplings for the four possible ground states in C_{2v} symmetry.

	Excited State Coupling		
Ground State	Δg_{xx}	Δg_{yy}	Δg_{zz}
X^2A_1	$^2B_2$	$^2B_1$	$^2A_2$
X^2A_2	$^2B_1$	$^2B_2$	$^2A_1$
X^2B_1	$^2A_2$	$^2A_1$	$^2B_2$
X^2B_2	$^2A_1$	$^2A_2$	$^2B_1$

Table 4. Calculated g-tensor data (Δg in ppm) for Ga_xAs_y (x + y = 3, 5), and comparison with experimental and other theoretical results.

	Δg_{xx}	Δg_{yy}	Δg_{zz}
$GaAs_2$ (X^2B_2)	175300	-175120	-18280
Ref. 13, calc.	95600	-116500	
Ga_2As (X^2B_2)	-125950	-24850	51030
Ref. 13, calc.	-188500	40100	
Ga_2As_3 (X^2A_2" in D_{3h})	-73410[a]	-	6460
Ref. 2, expt.	-82300	-	~ 0
Ref. 12, calc.	-148000	-	-16200
Ga_3As_2 (X^2A_1)	-71590	-11150	13270
$GaAs_4$ (X^2B_2)	-171030	-7540	-14720
Ga_4As (X^2A_1)	-123540	-21850	-43470

a Average of Δg_{xx} and Δg_{yy} from Table 7.

Table 5. Calculated values of ΔE, SO, L and Δg (2nd order) for excited states having a large magnetic coupling with the ground state of $GaAs_2$ (X^2B_2), and $^2B_2$ vertical excitation energies[a].

Component	ΔE (eV)	SO (cm^{-1})	L (au)	Δg (ppm)[b]
Δg_{xx} ($^2A_1$)				
1^2A_1 ($4a_1 \rightarrow 2b_2$, S-1 → S)[c]	1.47	169.5	1.096	64366
2^2A_1 ($3a_1 \rightarrow 2b_2$, S-3 → S)	2.67	475.1	1.105	99952
3^2A_1 ($1b_1 \rightarrow 1a_2$, S-2 → L)	2.89	165.1	0.149	4333
4^2A_1 ($2b_2 \rightarrow 5a_1$, S → L+3)	3.97	116.2	0.784	11687
5^2A_1 ($1b_1 \rightarrow 1a_2$, S-2 → L) [30%]	4.24	69.2	-0.404	-3357 **175300**
Δg_{yy} ($^2A_2$)				
1^2A_2 ($2b_2 \rightarrow 1a_2$, S → L)	1.26	476.4	-0.897	-172824
2^2A_2 ($4a_1 \rightarrow 2b_1$, S-1 → L+1)	3.19	98.4	0.872	13686
3^2A_2 ($4a_1 \rightarrow 2b_1$, S-1 → L+1)	3.90	-86.1	1.530	-17199
4^2A_2 ($3a_1 4a_1 \rightarrow 2b_2 1a_2$, S-3 + S-1 → S + L)	4.37	31.8	0.034	128
5^2A_2 ($4a_1^2 \rightarrow 2b_2 1a_2$, S-1 → S + L) [26%]	4.71	50.1	0.130	708 **-175120**
Δg_{zz} ($^2B_1$)				
1^2B_1 ($2b_2 \rightarrow 2b_1$, S → L+1)	2.27	-129.3	0.657	-19067
2^2B_1 ($1b_1 \rightarrow 2b_2$, S-2 → S)	2.55	36.5	-0.042	-307
3^2B_1 ($4a_1 \rightarrow 1a_2$, S-1 → L)	2.62	81.2	-0.033	-526
4^2B_1 ($4a_1 \rightarrow 1a_2$, S-1 → L) [57%]	3.13	250.8	-0.149	-6072
5^2B_1 ($3a_1 \rightarrow 1a_2$, S-3 → L)	3.61	348.0	0.983	48315
6^2B_1 ($3a_1 \rightarrow 1a_2$, S-3 → L)	3.89	190.9	-1.612	-40264 **-18280**

a The X^2B_2 ground state is ...$1b_2^2 1b_1^2 4a_1^2 2b_2^1$ (13 VE). Vertical excitation energies for 2^2B_2 to 5^2B_2 are 3.58, 4.25, 4.35, and 4.76 eV, respectively.

b Total contribution for all calculated excited states in boldface.

c S = SOMO, L = LUMO.

Table 6.Calculated values of ΔE, SO, L and Δg (2nd order) for excited states having a large magnetic coupling with the ground state of Ga_2As (X^2B_2), and $^2B_2$ vertical excitation energies[a].

Component	ΔE (eV)	SO (cm^{-1})	L (au)	Δg (ppm)[b]	
Δg_{xx} ($^2A_1$)					
1^2A_1 ($3a_1 \rightarrow 2b_2$, S-1 → S)[c]	0.17	177.4	-0.069	-36004	
2^2A_1 ($2b_2 \rightarrow 4a_1$, S → L) [58%]	1.97	243.5	-1.019	-64115	
3^2A_1 ($1b_1 \rightarrow 1a_2$, S-2 → L+1) [33%]	2.72	-60.7	0.735	-8368	
4^2A_1 ($3a_1^2 \rightarrow 2b_2 4a_1$, S-1 → S + L)	2.90	-204.4	0.910	-32678	
5^2A_1 ($1b_1 \rightarrow 1a_2$, S-2 → L+1)	3.38	-30.86	0.306	-1424	
6^2A_1 ($3a_1 \rightarrow 3b_2$, S-1 → L+3) [39%]	3.72	84.9	1.271	14761	**-125950**
Δg_{yy} ($^2A_2$)					
1^2A_2 ($1b_1 \rightarrow 4a_1$, S-2 → L)	2.32	2.7	0.154	91	
2^2A_2 ($2b_2 \rightarrow 1a_2$, S → L+1)	2.57	156.8	-0.477	-14834	
3^2A_2 ($1b_1 \rightarrow 4a_1$, S-2 → L)	2.78	41.9	0.014	108	
4^2A_2 ($3a_1 \rightarrow 2b_1$, S-1 → L+2) [39%]	3.32	158.5	-0.784	-19071	
5^2A_2 ($3a_1 \rightarrow 2b_1$, S-1 → L+2)	3.82	100.8	0.737	9909	**-24850**
Δg_{zz} ($^2B_1$)					
1^2B_1 ($1b_1 \rightarrow 2b_2$, S-2 → S)	0.33	254.7	0.219	87664	
2^2B_1 ($1b_1 3a_1 \rightarrow 2b_2 4a_1$, S-2 + S-1 → S + L)	2.57	-0.2	0.140	-4	
3^2B_1 ($3a_1 \rightarrow 1a_2$, S-1 → L+2)	2.66	122.2	0.904	21148	
4^2B_1 ($1b_1 3a_1 \rightarrow 2b_2 4a_1$, S-2 + S-1 → S + L)	3.01	41.3	0.051	360	
5^2B_1 ($3a_1 \rightarrow 1a_2$, S-1 → L+2)	3.32	-220.1	1.066	-35932	
6^2B_1 ($2b_2 \rightarrow 2b_1$, S → L+2) [40%]	3.74	146.9	-1.052	-21056	**51030**

a The X^2B_2 ground state is ...$1b_2^2 1b_1^2 3a_1^2 2b_2^1$ (11 VE). Vertical excitation energies for 2^2B_2 to 5^2B_2 are 2.24,

2.65, 3.17, and 3.41 eV, respectively.

b Total contribution for all calculated excited states in boldface.

c S = SOMO, L = LUMO.

Table 7. Calculated values of ΔE, SO, L and Δg (2nd order) for excited states having a large magnetic coupling with the ground state of Ga_2As_3 (X^2B_1), and $^2B_1$ vertical excitation energies[a].

Component	ΔE (eV)	SO (cm^{-1})	L (au)	Δg (ppm)[b]	
Δg_{xx} ($^2A_1$)					
1^2A_1 ($5a_1 \rightarrow 3b_1$, S-3 → S)[c]	1.98	41.5	-0.037	-398	
2^2A_1 ($4a_1 \rightarrow 3b_1$, S-5 → S)	2.98	0.4	-0.014	-1	
3^2A_1 ($3b_1 \rightarrow 6a_1$, S → L)	3.30	342.9	-1.777	-94074	
4^2A_1 ($3a_1 \rightarrow 3b_1$, S-6 → S)	3.87	0.02	0.003	0	
5^2A_1 ($3b_1 \rightarrow 7a_1$, S → L+4)	3.70	246.7	0.634	21549	
6^2A_1 ($1a_2 \rightarrow 4b_2$, S-2 → L+2)	3.43	148.1	0.396	8742	
7^2A_1 ($1a_2 \rightarrow 4b_2$, S-2 →L+2)	2.29	133.4	-0.368	-10911	**-75230**
Δg_{yy} ($^2B_2$)					
1^2B_2 ($2b_2 \rightarrow 3b_1$, S-4 → S)	2.69	-40.5	0.037	-284	
2^2B_2 ($3b_1 \rightarrow 3b_2$, S → L+1)	3.28	-355.5	1.761	-97100	
3^2B_2 ($3b_1 \rightarrow 4b_2$, S → L+2)	3.50	4.9	0.032	23	
4^2B_2 ($3b_1 \rightarrow 5b_2$, S → L+3)	3.67	269.0	0.713	26635	
5^2B_2 ($2b_1 \rightarrow 4b_2$, S-1 → L+2)	3.83	101.8	0.316	4287	
6^2B_2 ($2b_1 \rightarrow 4b_2$, S-1 → L+2)	3.93	119.2	-0.342	-5280	**-71590**

Δg_{zz} ($^2A_2$)					
1^2A_2 ($1a_2 \rightarrow 3b_1$, S-2 → S)	1.58	-0.1	$3x10^{-4}$	0	
2^2A_2 ($5a_1 \rightarrow 4b_2$, S-3 → L+2)	3.64	0.9	$6x10^{-5}$	0	
3^2A_2 ($4a_1 \rightarrow 4b_2$, S-5 → L+2)	2.89	71.8	0.401	5083	
4^2A_2 ($3b_1 \rightarrow 2a_2$, S → L+7)	4.55	0.3	$2x10^{-4}$	0	
5^2A_2 ($5a_1 \rightarrow 4b_2$, S-3 → L+2)	3.85	0.7	-0.021	-2	
6^2A_2 ($5a_1 \rightarrow 5b_2$, S-3 → L+3) [50%]	4.09	194.5	0.084	2041	**6460**

a The X^2B_2 ground state is $...2b_2^2 5a_1^2 1a_2^2 2b_1^2 3b_1^1$ (21 VE). Vertical excitation energies for 2^2B_1 to 5^2B_1 are 1.58, 3.85, 4.54, and 4.50 eV, respectively.

b Total contribution for all calculated excited states in boldface.

c S = SOMO, L = LUMO.

Table 8. Calculated values of ΔE, SO, L and Δg (2^{nd} order) for excited states having a large magnetic coupling with the ground state of Ga_3As_2 (X^2A_1), and $^2A_1$ vertical excitation energies[a].

Component	ΔE (eV)	SO (cm^{-1})	L (au)	Δg (ppm)[b]	
Δg_{xx} ($^2B_2$)					
1^2B_2 ($2b_2 \rightarrow 5a_1$, S-1 → S)[c]	0.72	-72.2	0.525	-26906	
2^2B_2 ($1a_2 \rightarrow 3b_1$, S-2 → L+2)	1.87	5.1	0.038	53	
3^2B_2 ($5a_1 \rightarrow 3b_2$, S → L) [48%]	2.94	221.4	-1.402	-53718	
4^2B_2 ($1a_2 \rightarrow 3b_1$, S-2 → L+2)	2.52	46.7	-0.653	-6177	
5^2B_2 ($2b_2 \rightarrow 6a_1$, S-1 → L+1) [52%]	2.94	22.2	-0.921	-3537	
6^2B_2 ($2b_2 \rightarrow 6a_1$, S-1 → L+1)	3.16	72.1	1.605	18664	**-71590**
Δg_{yy} ($^2B_1$)					
1^2B_1 ($2b_1 \rightarrow 5a_1$, S-3 → S)	1.15	80.3	0.902	32076	
2^2B_1 ($1a_2 \rightarrow 3b_2$, S-2 → L)	2.52	41.2	-0.783	-6518	
3^2B_1 ($5a_1 \rightarrow 3b_1$, S → L+2)	2.94	320.5	-0.599	-33328	
4^2B_1 ($1a_2 \rightarrow 3b_2$, S-2 → L)	2.58	15.3	-0.506	-1530	
5^2B_1 ($2b_1 \rightarrow 6a_1$, S-3 → L+1)	3.90	24.8	0.567	1840	
6^2B_1 ($4a_1 \rightarrow 3b_1$, S-4 → L+2)	2.50	-79.7	0.511	-8297	
11^2B_1 ($5a_1 \rightarrow 4b_1$, S → L+3)	4.34	71.2	0.955	7981	
14^2B_1 ($3a_1 \rightarrow 3b_1$, S-5 → L+2) [26%]	4.20	73.5	-0.732	-6536	**-11150**

Δg_{zz} ($^2A_2$)					
1^2A_2 ($1a_2 \rightarrow 5a_1$, S-2 → S)	1.00	76.5	0.394	15339	
2^2A_2 ($2b_2 \rightarrow 3b_1$, S-1 → L+2)	2.73	253.8	0.252	11927	
3^2A_2 ($2b_2 \rightarrow 3b_1$, S-1 → L+2)	2.79	75.3	-1.121	-15409	
4^2A_2 ($1a_2 \rightarrow 6a_1$, S-2 → L+1)	3.05	20.8	0.630	2191	
5^2A_2 ($1a_2 \rightarrow 6a_1$, S-2 → L+1)	2.92	2.7	-0.415	-200	**13270**

a The X^2A_1 ground state is ...$4a^{12}2b_1^{2}1a_2^{2}2b_2^{2}5a_1^{1}$ (19 VE). Vertical excitation energies for 2^2A_1 to 5^2A_1 are 1.68, 2.18, 2.56, and 2.90 eV, respectively.

b Total contribution for all calculated excited states in boldface.

c S = SOMO, L = LUMO.

Table 9. Calculated values of ΔE, SO, L and Δg (2^{nd} order) for excited states having a large magnetic coupling with the ground state of $GaAs_4$ (X^2B_2), and $^2B_2$ vertical excitation energies.

Component	ΔE (eV)	SO (cm^{-1})	L (au)	Δg (ppm)[b]	
Δg_{xx} ($^2A_1$)					
1^2A_1 ($3b_2 \rightarrow 6a_1$, S → L)[c]	0.55	390.3	-0.496	-179018	
2^2A_1 ($5a_1 \rightarrow 3b_2$, S-1 → S)	2.22	-249.0	1.0471	-59761	
3^2A_1 ($3b_2 \rightarrow 7a_1$, S → L+4)	2.46	171.5	0.070	2501	
4^2A_1 ($2b_2 \rightarrow 6a_1$, S-3 → L)	2.82	265.0	0.7923	37977	
5^2A_1 ($2b_2 \rightarrow 6a_1$, S-3 → L) [64%]	2.61	-139.8	0.386	-10558	
9^2A_1 ($5a_1 \rightarrow 4b_2$, S → L+1) [39%]	4.10	162.8	1.850	37462	**-171030**
Δg_{yy} ($^2A_2$)					
1^2A_2 ($3b_1 \rightarrow 6a_1$, S-2 → L)	1.91	-311.7	0.807	-66989	
2^2A_2 ($3b_1 \rightarrow 6a_1$, S-2 → L)	2.32	162.1	1.378	49104	
3^2A_2 ($3b_2 \rightarrow 2a_2$, S → L+5)	3.06	-188.6	0.117	-3699	
4^2A_2 ($2b_1 \rightarrow 6a_1$, S-4 → L)	3.37	336.6	0.057	-2937	
5^2A_2 ($2b_1 \rightarrow 6a_1$, S-4 → L)	3.18	129.2	0.794	16423	
6^2A_2 ($5a_1 \rightarrow 4b_1$, S-1 → L+3)	2.91	123.4	-0.372	-8027	
7^2A_2 ($3b_1 \rightarrow 7a_1$, S-2 → L+4)	3.44	111.3	-0.321	-5292	
9^2A_2 ($1a_2 \rightarrow 3b_2$, S-5 → S)	3.78	49.5	-0.355	-2363	
10^2A_2 ($3b_1 \rightarrow 7a_1$, S-2 → L+4)	4.43	83.0	1.561	14898	
11^2A_2 ($5a_1 \rightarrow 4b_1$, S-1 → L+3) [55%]	3.67	84.2	-0.494	-5790	
13^2A_2 ($3b_1 3b_2 \rightarrow 6a_1 5b_2$, S-2 + S → L + L+2) [28%]	3.66	70.5	0.702	6890	**-7540**

Δg_{zz} ($^2B_1$)					
1^2B_1 ($3b_1 \rightarrow 3b_2$, S-2 → S)	1.90	285.7	0.777	59501	
2^2B_1 ($3b_2 \rightarrow 4b_1$, S → L+3)	2.57	-259.9	1.285	-66074	
3^2B_1 ($3b_1 3b_2 \rightarrow 6a_1^2$, S-2 + S → L)	2.40	163.7	0.200	6966	
4^2B_1 ($2b_1 \rightarrow 3b_2$, S-4 → L)	3.10	293.5	0.102	4943	
5^2B_1 ($3b_1 \rightarrow 4b_2$, S-2 → L+1)	3.19	-63.2	0.765	-7720	
6^2B_1 ($3b_2 \rightarrow 5b_1$, S → L+6) [58%]	2.54	-79.2	0.921	-14645	
8^2B_1 ($3b_1 \rightarrow 5b_2$, S-2 → L+2)	3.67	-118.9	1.378	-22751	
11^2B_1 ($3b_1 \rightarrow 5b_2$, S-2 → L+2)	3.72	114.4	1.319	20686	**-14720**

a The X^2B_2 ground state is $...1a_2^2 2b_2^2 3b_1^2 5a_1^2 3b_2^1$ (23 VE). Vertical excitation energies for 2^2B_2 to 5^2B_2 are 1.62, 2.60, 2.54, and 2.63 eV, respectively.

b Total contribution for all calculated excited states in boldface.

c S = SOMO, L = LUMO.

Table 10. Calculated values of ΔE, SO, L and Δg (2nd order) for excited states having a large magnetic coupling with the ground state of Ga_4As (X^2A_1), and $^2A_1$ vertical excitation energies[a].

Component	ΔE (eV)	SO (cm^{-1})	L (au)	Δg (ppm)[b]	
Δg_{xx} ($^2B_2$)					
1^2B_2 ($5a_1 \rightarrow 4b_2$, S → L+1)[c] [62%]	1.28	223.4	-1.224	-108538	
2^2B_2 ($5a_1 \rightarrow 4b_2$, S → L+1) [29%]	1.59	-51.6	1.4029	-23187	
3^2B_2 ($2b_2 \rightarrow 5a_1$, S-4 → S)	2.73	-24.1	1.423	-6406	
4^2B_2 ($1b_1 \rightarrow 1a_2$, S-3 → L)	2.98	6.6	-0.664	-751	
5^2B_2 ($1b_1 \rightarrow 1a_2$, S-3 → L) [46%]	3.02	-23.0	-0.147	572	**-123540**
Δg_{yy} ($^2B_1$)					
1^2B_1 ($5a_1 \rightarrow 2b_1$, S → L+2)	1.45	-18.1	0.216	-1378	
2^2B_1 ($1b_1 \rightarrow 5a_1$, S-3 → S)	2.23	47.8	-0.041	-457	
3^2B_1 ($3b_2 \rightarrow 1a_2$, S-1 → L)	2.03	-1.6	0.148	-61	
4^2B_1 ($3b_2 \rightarrow 1a_2$, S-1 → L)	2.44	-30.0	0.224	-1405	
5^2B_1 ($4a_1 \rightarrow 2b_1$, S-2 → L+2)	2.75	249.0	0.0782	3601	
6^2B_1 ($4a_1 \rightarrow 2b_1$, S-2 → L+2)	2.92	-30.7	1.616	-8668	
7^2B_1 ($5a_1 \rightarrow 3b_1$, S → L+3)	3.06	-72.1	0.724	-8675	
8^2B_1 ($2b_2 \rightarrow 1a_2$, S-4 → L)	2.99	-24.6	1.409	-5893	**-21850**

Δg_{zz} ($^2A_2$)					
1^2A_2 ($5a_1 \rightarrow 1a_2$, S → L)	1.22	-63.9	0.256	-6838	
2^2A_2 ($4a_1 \rightarrow 1a_2$, S-2 → L)	2.49	-0.06	0.357	-5	
3^2A_2 ($4a_1 \rightarrow 1a_2$, S-2 → L)	2.62	12.7	-0.105	-262	
4^2A_2 ($3b_2 \rightarrow 2b_1$, S-1 → L+2)	2.42	-43.5	-0.432	3948	
5^2A_2 ($1b_1 \rightarrow 4b_2$, S-3 → L+1)	2.93	7.1	-0.049	-62	
6^2A_2 ($3b_2 \rightarrow 2b_1$, S-1 → L+2)	3.44	215.6	-0.422	-13477	
7^2A_2 ($5a_1 \rightarrow 2a_2$, S → L+5) [41%]	3.26	205.7	-0.451	-14511	
11^2A_2 ($3b_2 \rightarrow 3b_1$, S-1 → L+3) [42%]	3.83	102.7	0.847	11592	
12^2A_2 ($3b_2 \rightarrow 3b_1$, S-1 → L+3) [60%]	3.96	-63.9	1.277	-10487	
14^2A_2 ($2b_2 \rightarrow 2b_1$, S-4 → L+2)	3.98	-39.4	1.652	-8334	**-43470**

a The X^2A_1 ground state is ...$1b_1^2 4a_1^2 3b_2^2 5a_1^1$ (17 VE). Vertical excitation energies for 2^2A_1 to 5^2A_1 are 1.66, 2.79, 2.80, and 3.02 eV, respectively.

b Total contribution for all calculated excited states in boldface.

c S = SOMO, L = LUMO.

Captions for figures:

Figure 1. Optimized geometries of Ga_xAs_y ($x + y = 3, 5$) isomers, shown in increasing relative energy from left to right. Bond lengths and angles given in Table 1.